\( ^{13}\text{C NMR} \)

The \(^{13}\text{C NMR} \) is generated in the same fundamental way as proton NMR spectrum. Only 1.1 % of naturally occurring carbon is \(^{13}\text{C} \) and actually an advantage because of less coupling.

**Requirement for NMR:** Spin quantum # (I) ≠ 0 Meaning → must be an odd number and/or neutrons. Ex. \(^{1}\text{H}, ^{2}\text{H}, ^{13}\text{C}, ^{19}\text{F}, \text{etc}…("\text{Thinkbook}"\)
How do we find this? Look at the atomic number.

The \(^{13}\text{C} \) NMR is directly about the carbon skeleton not just the proton attached to it.

a. The **number of signals** tell us how many different carbons or set of equivalent carbons

b. The **splitting of a signal** tells us how many hydrogens are attached to each carbon. (N+1 rule)

c. The **chemical shift** tells us the hybridization (sp\(^3\), sp\(^2\), sp) of each carbon.

d. Integration: Not useful for \(^{13}\text{C} \) NMR

**Proton –coupled spectrum** shows splitting of the carbon signal only by protons attached to *that* carbon *itself*.

\(^{13}\text{C}_\text{H coupling} \) not \(^{13}\text{C}_\text{C}_{-}^{13}\text{C}_\text{H} \) or not \(^{13}\text{C}_\text{C}_{-}^{13}\text{C}_\text{C}_{-}^{13}\text{C}_\text{H} \) or not \(^{12}\text{C}_\text{C}_{-}^{13}\text{C} \)

Coupling occurs but very low due to low abundance 1.1 %x 1.11% No coupling \(^{12}\text{C} I=0 \)

("\text{Thinkbook}"")

Thus, for each carbon the multiplicity of the signal depends upon how many protons are attached to it.

**Note:** Due to low natural abundance, \(^{13}\text{C} \) NMR spectra do not ordinarily show carbon-carbon splitting two \(^{13}\text{C} \) being next to other is 1.1 %x 1.1%=0.012 % (because \(^{12}\text{C} \) does not have a magnetic moment, it cannot split the signal of an adjacent \(^{13}\text{C} \), and are thus enormously simplified. ("\text{Thinkbook}"\)

**Proton-Decoupled Spectrum** shows no splitting at all; it consists of a set of single peaks, one for each carbon or each set of equivalent carbons in a molecule. Even for very complicated molecules, such a spectrum is amazingly simple (because overlapping multiplets very difficult to interpret)-most commonly run spectrum for structural analysis; and will list the multiplicity of the peaks in the upper left-hand corner. (Bruice)

**Chemical Shift** in \(^{13}\text{C} \) NMR spectrum arises in the same way as in the proton NMR spectrum. Each carbon nucleus has its own electronic environment, different from the environment of other, non-equivalent nuclei; it feels a different magnetic field, and absorbs at different applied fields strength.

- Electronegative atoms and pi bonds cause downfield shifts ("\text{Thinkbook}"\)
- \(^{13}\text{C} \) chemical shift range 0-250 ppm ("\text{Thinkbook}"\)
In $^{13}$C NMR spectrum, the more electronegative group bonded to carbon atom $\rightarrow$ deshielding increases. This table demonstrates this effect.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>Br</th>
<th>Cl</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity (Pauling Scale)</td>
<td>2.5</td>
<td>2.8</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Sp$^3$ hydrid carbon</td>
<td>CH$_3$I</td>
<td>CH$_3$Br</td>
<td>CH$_3$Cl</td>
<td>CH$_3$F</td>
</tr>
<tr>
<td>Chemical shift (ppm)</td>
<td>9.6</td>
<td>25.6</td>
<td>49.9</td>
<td>71.6</td>
</tr>
</tbody>
</table>

How many signals are in the $^{13}$C NMR spectrum?

$\text{CH}_3 \_ \text{CH}_2 \_ \text{CH}_2 \_ \text{CH}_2 \_ \text{CH}_2 \_ \text{CH}=\text{CH}_2$

Eight signals, no equivalent carbons

Determine the structure from this formula C$_4$H$_8$O$_2$ in 13 spectrum $\rightarrow$ 179.9 ppm (triplet)
51.5 ppm (quartet), 27.5 ppm (triplet) and 9.2 ppm (quartet) ("Thinkbook PP#12")
179.9 ppm corresponding to ester or ketone carbonyl group; 51.5 ppm is downfield must
be close to carbonyl or oxygen (OCH$_3$); 27.5 ppm (CH2) and 9.2 ppm (quartet) –CH$_3$
group further away from carbonyl group in upfield region.
These are three structures possibilities:

CH$_3$—C—OCH$_2$—CH$_3$  \hspace{1cm} CH$_3$—CH$_2$C—O—CH$_3$  \hspace{1cm} CH$_3$—C—CH$_2$—O—CH$_3$
Methyl propionate    \hspace{1cm} \hspace{1cm} \hspace{1cm} a \hspace{0.5cm} b \hspace{0.5cm} c \hspace{0.5cm} d
Note: b. this C must downfield and probably over 200 ppm.
Actual structure = Methyl Propionate (\textsuperscript{13}C spectrum above)

\[\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{C} \text{CH}\]

Six signals (no equivalent carbons)

\[\begin{array}{cccccc}
13.7 & 22.1 & 30.9 & 18.3 & 84.5 & 68.4 \\
\end{array}\]

(\text{note: there are six carbons but} \text{\textsuperscript{13}}\text{C NMR showed only 3 signals})

\[\begin{array}{cccccc}
a & a & b & b & c & c \\
ak. 14.16 \text{ppm} & b. 31.87 \text{ppm} & c. 22.89 \text{ppm} & \text{due to molecular symmetry}\n\end{array}\]
Cyclohexane has one signal because all carbons on the ring are equivalent carbons.

**Note:** Enantiomers and resonance contributors have identical spectra but diastereomers spectra are NOT identical.

**Typical 13C NMR Chemical Shift ranges**

<table>
<thead>
<tr>
<th>ppm</th>
<th>Hybridization</th>
<th>Kinds of compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-70</td>
<td>Sp³</td>
<td>Alkane (CH₃)</td>
</tr>
<tr>
<td>70-100</td>
<td>Sp³ and sp</td>
<td>C-O and C-N</td>
</tr>
<tr>
<td>100-160</td>
<td>Sp²</td>
<td>Aromatic C and C=C</td>
</tr>
<tr>
<td>160-210</td>
<td>Sp²</td>
<td>Aldehydes and ketone carbonyl (C=O)</td>
</tr>
</tbody>
</table>

**Splitting Pattern** (N+1 rule): for each carbon the multiplicity of the signal depends upon how many protons are attached to it.

Ex. \[ \text{H} \]

\[ \_C\_ \quad \text{H} \quad _C_ \quad \text{H} \quad _C_ \quad \text{H} \quad _C_ \quad \text{H} \quad _C_ \]

- no proton singlet
- one proton doublet
- two protons triplet
- three protons quartet

2D- NMR: Interaction of nuclear spins plotted in two dimensions. Correlation Spectroscopy (COSY)
- Two axes correspond to the single isotope “Thinkbook”
- The interaction indicates with H’s are coupled gives better understanding of structure. (“Thinkbook”)
Heteronuclear Multiple-Quantum Coherence (HMOC)

- 2 axes correspond to 2 different isotopes (usually $^{13}\text{C}$ and $^{1}\text{H}$)
- Interaction indicates H’s coupling to nuclei other than H

Magnetic Resonance Imaging (MRI)

- $^{1}\text{H}$ NMR spectroscopy has been applied to diagnostic medicine.
- The relaxation times of hydrogen atoms in different environments (ex. brain vs. bone)
- The rate of relaxation is related to the extent of binding of water to the surface of biological molecules.

*Note: These $^{13}\text{C}$ spectra obtained from National Institute of Advanced Science and Technology (AISt) website: [http://www.aist.go.jp/](http://www.aist.go.jp/)*